Catalytic Oxidation of Short Chain Hydrocarbons and Selective Catalytic Reduction of Nitrogen Oxides on Supported Palladium Catalysts

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By

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Abstract

Lean burn engine exhausts contain several undesirable chemical species that are often released into the environment. These pollutants include considerable amounts of nitrogen oxides (NO_x), unburnt hydrocarbons, and carbon monoxide. These species are known precursors to acid rain, smog and ground level ozone formation. In order to comply with stringent environmental regulations, a selective catalytic reduction (SCR) system is designed to reduce these emissions under lean conditions. Industrial engines typically operate in these oxygen-rich conditions to combust as much of the fuel as possible, which minimizes pollution by hydrocarbons. This dual catalyst bed promotes the oxidation of NO to NO_2 and the subsequent reduction of NO_2 with hydrocarbons to diatomic nitrogen, water, and carbon dioxide. Past research of Dr. Ozkan's research group at The Ohio State University has been focused on using palladium on sulfated zirconia (Pd/SZ) as the reduction catalyst and cobalt oxide on ceria (CoO_x/CeO_2) as the oxidation catalyst [1].

This study is interested in the use of the palladium catalyst to reduce nitrogen oxides in the presence of short chain hydrocarbons that are not burned in the combustion process of the engine, namely methane and propane. This is done by passing a known feed designed to simulate the products of combustion through a packed bed of this catalyst. Since this reaction is known to be inhibited by the presence of water, trials with and without water are performed for comparison. Supports of interest to this study include sulfated zirconia, which has been used previously, as well as a new material known as osorb (Oz). This material has several novel characteristics that make it a

desirable support for this reaction. Most notably, osorb is a highly hydrophobic material [2]. It is expected to reject water from accessing the active sites, thus reducing the impact that water has on the activation of these light alkanes. These catalysts are also tested for their ability to reduce NO_2 while using the alkanes as reducing agents.

Both catalysts of interest were shown to have the ability to reduce NO_2 with both methane and propane. As expected, conversions of methane were lower than that of propane due to the lack of a carbon-carbon bond. Water was shown to have an effect on the conversion of methane on both catalysts, as well as on the conversion of propane on the Pd/SZ catalyst. The Pd/Oz support showed no difference in conversion of propane. However, conversions seen on the Pd/SZ catalyst were generally greater than those seen on the Pd/Oz catalyst. Additional synthesis and experimentation may be required on this new support to best tailor its qualities for this reaction.

Dedication

This document is dedicated to my father, who sparked my interest in chemistry and chemical engineering at a young age. He has helped me find my academic passions, encouraged my work, and offered countless thought provoking conversations.

Acknowledgments

A great deal of thanks and appreciation is given to Dr. Umit Ozkan, Sreshtha Sinha Majumdar, Gökhan Çelik, and all other members of the Heterogeneous Catalysis Research Group for their teaching and guidance.

Vita

June 2010 …….. William Mason High School

Fields of Study

Major Field: Chemical and Biomolecular Engineering

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Introduction

The use of hydrocarbons as the reducing agent(s) for selective catalytic reduction (SCR) of NO_x gases has many benefits to both processing and the environment. The following reactions are the desired steps of SCR by this method.

$$NO + \frac{1}{2}O_2 \rightarrow NO_2$$

$$NO_2 + C_xH_y \rightarrow N_2 + CO_2 + H_2O$$

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

$$C_xH_y + O_2 \rightarrow CO_2 + H_2O$$

Traditionally, either ammonia or urea has been used as the reducing agent for the reduction of NO_2. While these compounds are good reducing agents, several problems exist with their use. These include direct oxidation of ammonia, ammonia slip, and formation of ammonia salts that corrode downstream equipment [3]. There are additional disadvantages related to the initial and working capital costs of supplying these chemicals to a SCR unit. Another class of pollutants often released from combustion processes is unburnt hydrocarbons. With recent developments surrounding the abundance of natural gas in the United States, this fuel source will likely be utilized for several decades in industrial applications while its cost is low. Figure 1 shows the projected electricity generation by natural gas and coal over the next several decades.

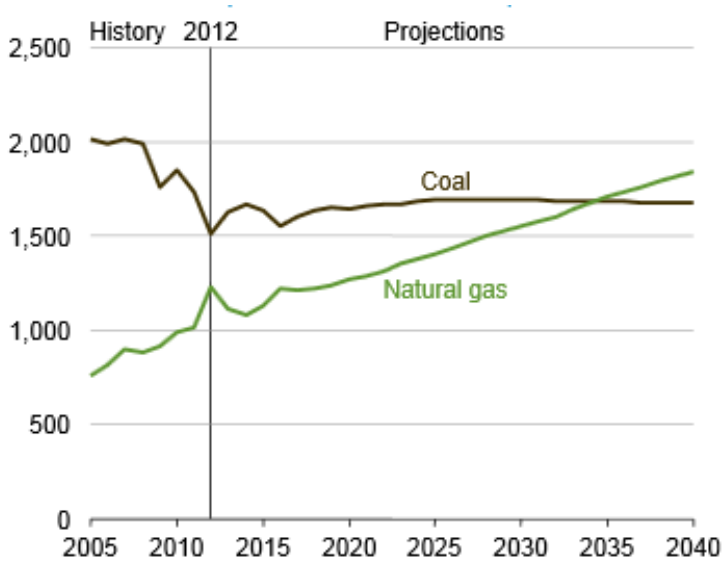

Figure 1: Natural Gas Energy Production Predictions

Due to this boom in electricity production via natural gas, selective catalytic reduction with these lighter hydrocarbons is highly desirable. Natural gas is primarily made of methane (75%-90%) with a balance of ethane, propane, and higher hydrocarbons [5]. Even under lean burn conditions, small amount of unburnt hydrocarbons will still be emitted by industrial engines. For these reasons, research is being performed to use these hydrocarbons as reducing agents for the reduction of NO_x. This eliminates the need to supply an external reducing agent to the selective catalytic reduction process. Unfortunately, this causes many new challenges, most notably surrounding the activation of these compounds on metal catalysts.

Although carbon dioxide is a known greenhouse gas, the other pollutants present in the combustion effluent gas (NO_x and hydrocarbons) are known to be much worse for the environment. The United States Environmental Protection Agency (EPA) has determined a global warming potential (GWP) for many known pollutants, including

these compounds. This value is a rating of how dangerous these molecules may be to the environment over a 100 year period. Carbon dioxide is used as a basis and assigned a GWP of 1. For comparison, methane and nitrous oxide (N_2O) are assigned GWP values of 21 and 310, respectively [6]. The current standard for NO_2 is set at 53 ppb. This standard has been in place since the inception of the Clean Air Act in 1971. As of 2012, the US EPA was considering changing the monitoring requirements to ensure that this standard is being met across the country [7]. As energy demand increases, more fuel must be burned with current technologies to meet this demand. This directly increases the emissions from power plants that use natural gas as a fuel source. Due to the environmental hazards associated with NO_x and hydrocarbons, reducing these emissions is worth pursuing for the benefit of society. Technologies currently being studied for the use of carbon capture may be later employed downstream of a selective catalytic reduction unit to further reduce carbon dioxide emissions.

This study is interested in the catalytic oxidation of methane and propane to water and carbon dioxide, as well as the reduction of NO_2 to nitrogen, water, and carbon dioxide with these same alkanes. These reactions are to be carried out on the palladium catalyst. Several different variables are tested in this study for their impact on the ability of this catalyst to oxidize either methane or propane. These include reaction temperature, feed water content, and the support used with the palladium metal. The ultimate goal is to develop catalysts that drive these reactions with high conversions of the hydrocarbons and nitrogen oxides while maintaining stability of the palladium catalyst.

Literature Review

The complete oxidation of methane has been shown by several independent groups to be first order in the concentration of methane and zero order in the concentration of oxygen [8]. Ribeiro et al. have previously studied the kinetics of the complete oxidation of methane with the use of a palladium catalyst. On this catalyst, it was determined that the presence of water inhibited the oxidation reaction. The reaction order for this species was found to be -1. The effect of carbon dioxide on the reaction rate was also studied. It was found that for concentrations below 5% by volume, the reaction rate showed no dependence on the concentration of carbon dioxide. However, once this threshold was reached, the reaction order became -2 [9].

While there are many advantages to using methane as a reducing agent in a selective catalytic reduction system, the primary technical challenge is still yet to be fully overcome. When longer hydrocarbons are used in these reactions, the carbon-carbon bonds are utilized as they are the easiest bond to break in an alkane. Since there are no such bonds in methane, this molecule is more difficult activate [8]. Palladium has been shown to be the most active metal for the catalytic combustion of methane. Specifically, palladium oxide (PdO) has been shown to be the active site for this reaction. This site is prone to being poisoned by sulfur compounds that form $PdSO_4$ [10]. Previous work in Dr. Ozkan's research group has shown that conversion of methane over the dual catalyst bed (Pd/SZ and CoO/CeO) at 20% while conversion of propane is 100% under the same conditions [3]. This further illustrates the difference in activity between methane and propane on the Pd/SZ catalyst.

Sulfated zirconia is a commonly used support for palladium in this catalyst. It has been previously reported that this support has given the highest activity for NO_x reduction with a palladium catalyst [11]. However, this reaction is still inhibited by water and conversion of NO_x in the presence of water has been shown to decrease with time [12].

Catalyst Synthesis

0.3% Palladium on Sulfated Zirconia

The Pd/SZ catalysts were synthesized with a one pot sol-gel technique. Palladium acetate and zirconium propoxide are used as precursors for this catalyst. First, palladium acetate is dissolved in n-propanol under air between 20°C and 25°C. Quick additions of zirconium propoxide and sulfuric acid are then performed. Sulfuric acid is the sulfating agent for this catalyst. Acetic acid is then used as the hydrolyzing agent and is added drop-wise to the solution. Once this addition is completed, the mixture is stirred and allowed to gel. When the mixture gels, it changes from a clear dark brown color to an opaque light brown. Figure 2 shows the catalyst before and after gelling is complete.

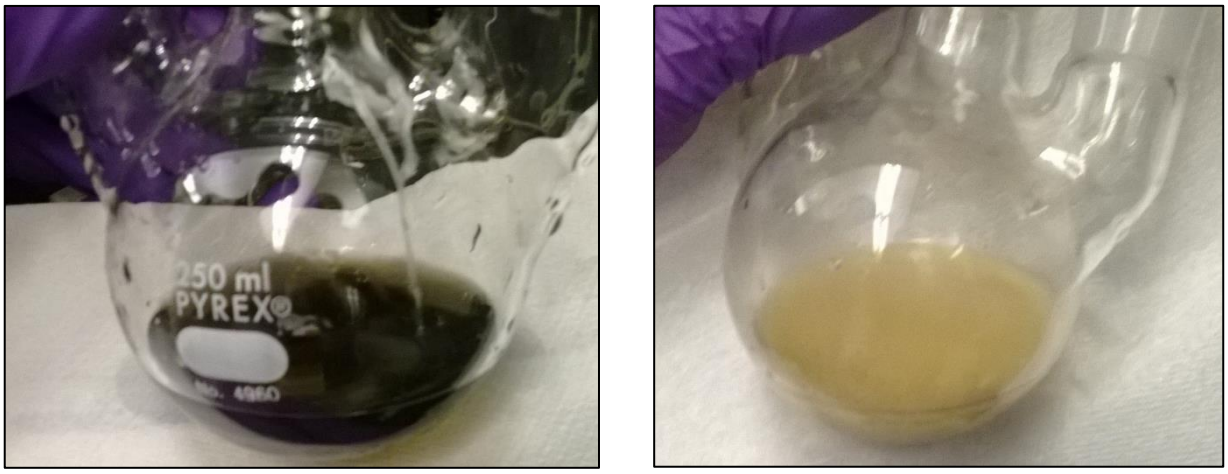

Figure 2: Pd/SZ Catalyst Before and After Gelling

The catalyst is then dried overnight at 110°C, resulting in an off-white solid. The catalyst is then calcined for 4 hours under air at 700°C with a ramp rate of 10°C/min. Palladium loadings of 0.3% are used in this study.

Palladium on Osorb

Swellable organically modified silica (SOMS) is a new material that is of current interest to this project as a catalyst support. This material is commonly referred to as osorb (Oz). This material has several interesting characteristics, most notably its ability to reversibly absorb organic compounds while rejecting water. This material may be regenerated as the absorption process is completely reversible [2]. Due to the hydrophobicity of this material, it may reduce the effect of water on complete oxidation of methane. This material is synthesized with a sol-gel method and aged for six days before being ground into the product [13]. In these experiments, the palladium catalyst is placed on the osorb with an incipient wetness impregnation procedure. Palladium acetate is first dissolved in acetone. Osorb is then added to the mixture and mixed with the solution. The excess acetone is then evaporated and this procedure is repeated three additional times. Finally, the material is calcined at 300°C. Two different types of osorb-supported catalysts are used in this study. The first is palladium on sulfated osorb, to which sulfate groups were added to the support by an organic sulfur precursor. The second is non-swellable osorb, which has all the same characteristics of the typical osorb material except for the ability to swell. The sulfated osorb catalysts are loaded with 10% palladium and the non-swellable osorb catalysts are loaded with 1% palladium.

Process Description and Operation

In this system, reaction gas flow rates are measured with several Brooks 5850E Series mass flow meters that are controlled by two Brooks mass flow controllers. Reaction gases are obtained from Praxair for use in this system. Mass balances are derived and solved to determine the required volumetric flow rates of each of the input gases. All feeds are balanced with helium. A bubble flow meter is then used to calibrate the mass flow controller set points to the desired volumetric flow rates. For runs in which water is added, the bubbler temperature required to saturate the reactant stream with the desired water content is calculated and controlled with a variac controller with attached thermocouple. Figure 3 shows the laboratory system.

Figure 3: Laboratory Selective Catalytic Reduction System

As seen in this figure, gas lines are insulated to prevent condensation on the lines. The Agilent 3000A Micro GC is connected to a computer (not pictured) that collects and stores the data collected by the GC. A more detailed process diagram is included as Figure 4.

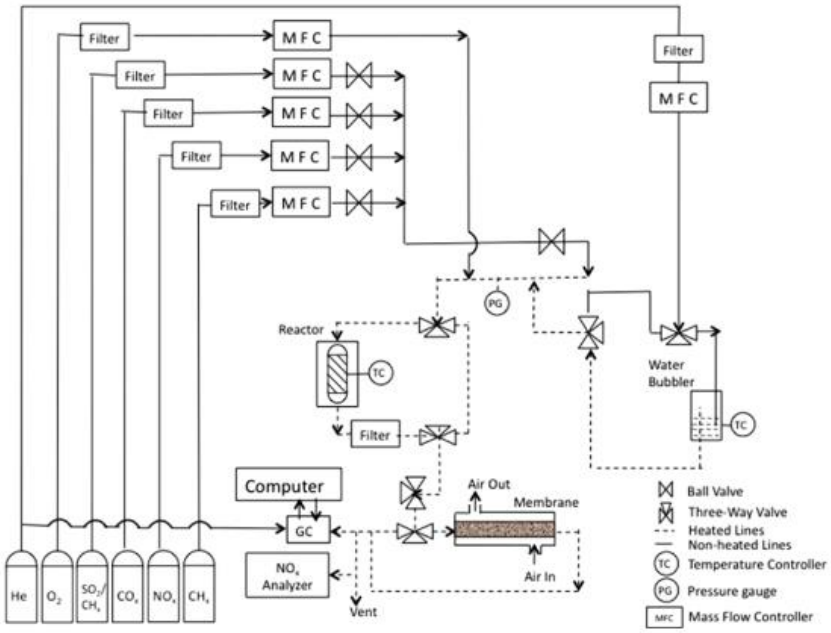

Figure 4: P&ID of Laboratory SCR System [3]

Once gas flow rates for each experiment have been calculated and calibrated, the catalyst is added along with quartz wool (for support) to the ¼ inch Swagelok tube reactor. The Osorb based catalyst sample is then reduced with 5% hydrogen in helium at 300 °C for 30 minutes and the palladium sulfated zirconia catalyst is oxidized with 10% oxygen in helium at 500°C for 30 min. At this point, the feed is allowed to pass through the Micro GC so that its composition can be verified and saved for later calculations. The reaction is then started at the lowest temperature of interest to the experiment with the

feed that does not include water ("dry run"). The reactants are passed through the catalyst bed until the areas reported by the Micro GC are stable. At this point, the flow configuration is modified to include water in the feed ("wet run") and the reaction is again allowed to reach steady state under the new conditions. Once this has occurred, the reaction temperature is increased to the next value of interest and the above procedure is repeated until all data has been collected.

Once all data has been collected, these data can be analyzed by several methods. First and foremost, the area measurements taken by the GC must be converted to parts per million (ppm) values. This is done with known response factors for each gas molecule. These values are summarized in Table 1.

Table 1: Response Factors of Molecules

Molecule	O_2	CH_4	C_3H_8	CO_2
Response Factor	0.256668	0.2819	0.56	0.81

Finally, conversion can be calculated for any species with Equation 1.

$$X_i = \frac{PPM_{i_{IN}} - PPM_{i_{OUT}}}{PPM_{i_{IN}}} \quad (1)$$

In Equation 1, X_i is the fractional conversion of species i. The feed analysis gives the inlet concentration values that are used in these calculations.

A MKS Cirrus mass spectrometer was used to obtain qualitative information on the reduction of NO_2 in these experiments. Signals produced by this instrument are analyzed for relative changes in composition of the product stream as compared to the feed.

Results and Analysis

Methane Oxidation on Pd/SZ

The palladium on sulfated zirconia was first tested under reaction conditions. This catalyst is known to be a good candidate for the oxidation of methane. A 0.3% Pd/SZ catalyst was made with the sol-gel synthesis procedure described previously. 200 mg of this catalyst, along with 100 mg of quartz powder and wool used to reduce pressure drop in the bed and to hold the catalyst in place, were packed into the reactor. Feed analysis was performed and the catalyst was reduced at 500°C under hydrogen. Data was collected with the Agilent 3000A Micro GC at temperatures from 400°C to 500°C in 10°C intervals for both dry and wet runs. Table 2 gives the feed flow rates of each component sent to the reactor.

Table 2: Feed Flow Rates over 0.3% Pd/SZ

Component	Composition
CH_4	16.9 ccm
O_2	10%
H_2O	7%
Total Flow	50 ccm

The water bubbler was controlled at a temperature of 51°C to achieve the above water feed rate. Tables A1 and A2 in Appendix A show the steady state areas collected by the Micro GC for methane and carbon dioxide along with corresponding concentrations (in ppm) and conversion of methane for the dry and wet runs. Figure 5 shows these conversions for both dry and wet runs as a function of temperature.

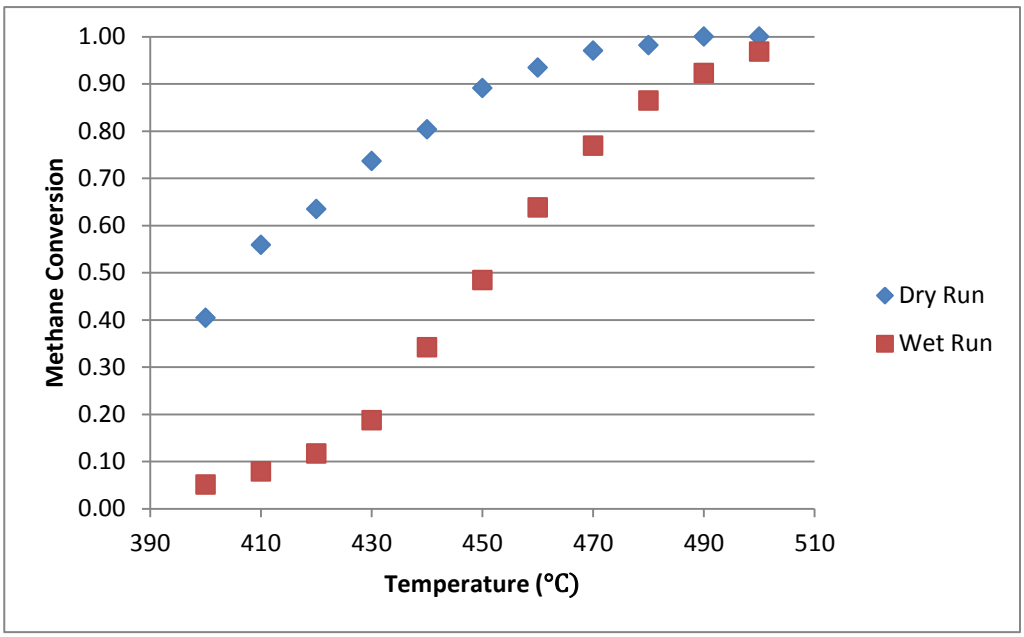

Figure 5: Experimental Conversion of Methane on 0.3% Pd/SZ

There is an obvious effect of water on the conversion of methane to carbon dioxide shown in this plot. To confirm, statistical analysis is performed in JMP to test if there is a significant difference between conversions in wet and dry runs. A paired t-test is used for this analysis on the following hypothesis:

$$H_o: X_d = X_w \qquad H_1: X_d \neq X_w$$

This test reported a p-value of <0.0001 was reported. This result indicates again that there is a significant difference in methane conversion between the wet and dry runs on this catalyst. The full printout may be seen in Figure B1.

Oxidation of Hydrocarbons and Reduction of NO_2 on Pd/SZ

Methane was investigated for its ability to also reduce NO_2 by introducing this gas into the feed. To measure nitrogen and NO_2 signals, a MKS Cirrus mass spectrometer (MS) was connected to the laboratory system such that the product gases would be sent first through the Micro GC, then to the MS. Table 3 shows the feed composition used in this experiment.

Table 3: Feed Composition for Pd/SZ NO_2 Reduction Experiment

Component	Composition
CH_4	2%
O_2	10%
NO_2	2014 ppm
H_2O	7%
Total	25 ccm

This reaction was carried out at temperatures from 450°C to 550°C in 50°C intervals. Methane conversion was calculated as was done with previous experiments. Data from the Micro GC, carbon dioxide and methane concentrations, and methane conversion are summarized in Tables A3 and A4. Methane conversion is plotted in Figure 6.

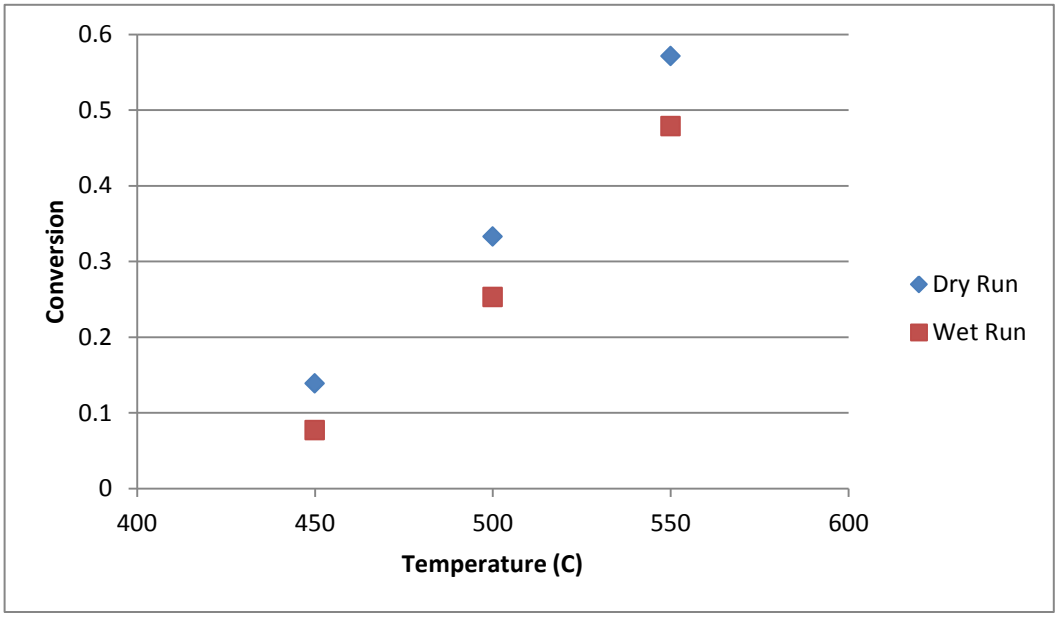

Figure 6: Fractional Conversion of Methane on 0.3% Pd/SZ with NO_2

A paired t-test was performed in JMP on these data to test if the presence of water had a significant effect on methane conversion. A p-value of 0.0064 is reported, indicating that the presence of water had a significant effect on the conversion of methane from 450°C to 550°C. A full printout of this test can be seen in Figure B2.

In this study, NO_2 is also introduced to the system to see if the catalyst can simultaneously oxidize propane to carbon dioxide and water while reducing NO_2 with methane to carbon dioxide, water, and nitrogen. In order to quantify the reduction of NO_2 in this system, the product stream was also passed through the MS for analysis. Figure 7 shows the nitrogen signal from the MS for the dry runs in this experiment.

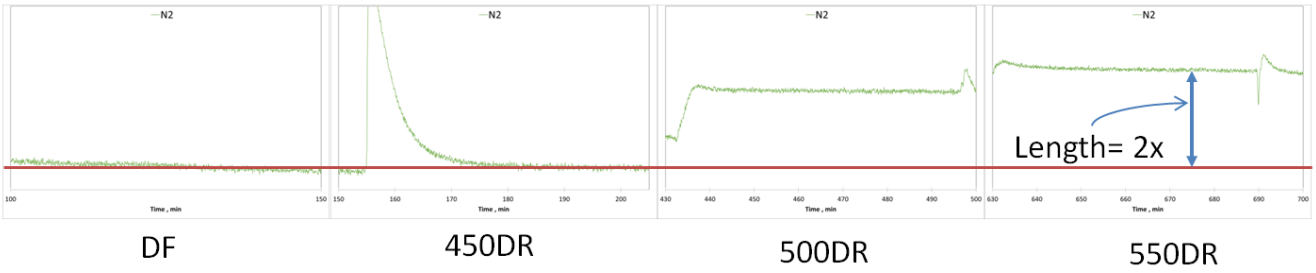

Figure 7: N_2 Signal for Dry Runs on 0.3% Pd/SZ with CH_4 and NO_2

The spike in the 450°C dry run data is a result of changing the system from performing the feed analysis to the dry run and can be neglected. The nitrogen signal seen in the 450°C dry run lies on the baseline, indicating that no nitrogen was produced at this temperature. The signal increases at 500°C and at 550°C, indicating that nitrogen was produced on this catalyst at these temperatures. Let the signal height of the final run be "2x" (in arbitrary units). This will be referenced later. These outputs suggest that NO_2 was reduced at the two higher temperatures tested, resulting in an increased nitrogen signal. Figure 8 shows the NO_2 signal measured by the MS.

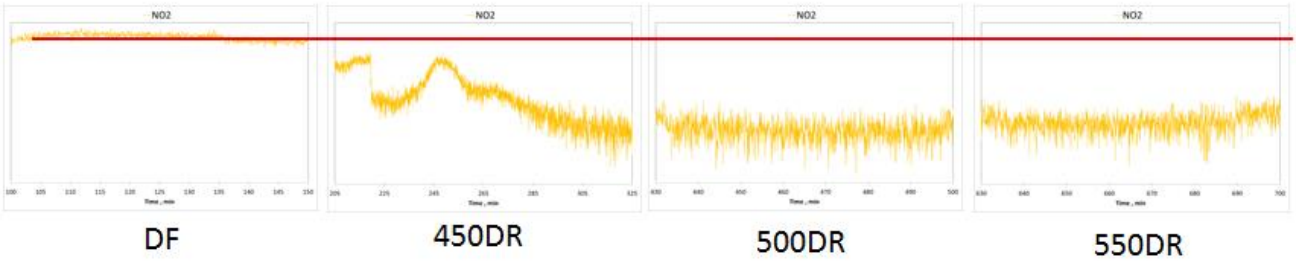

Figure 8: NO_2 Signal for Dry Runs on 0.3% Pd/SZ with CH_4 and NO_2

These plots show a decrease in the amount of NO_2 that remains in the products as temperature increases. This data shows that NO_2 is successfully being converted to

nitrogen on this catalyst. Additional quantitative measurements can be taken to determine the extent of this reaction.

Next, consider the wet runs performed in this experiment. Figure 9 shows the nitrogen signal from the wet runs in this experiment.

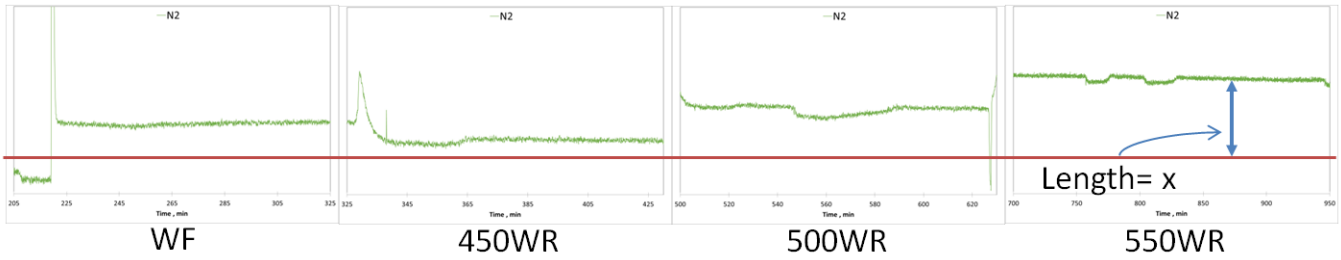

Figure 9: N_2 Signal for Wet Runs on 0.3% Pd/SZ with CH_4 and NO_2

Similar trends are seen in nitrogen production for the wet runs, but the total amount of nitrogen produced is approximately half of that generated by the dry runs. This indicates that NO_2 reduction may also be inhibited by the presence of water in the feed. Figure 10 shows the NO_2 signal produced by the MS for these runs.

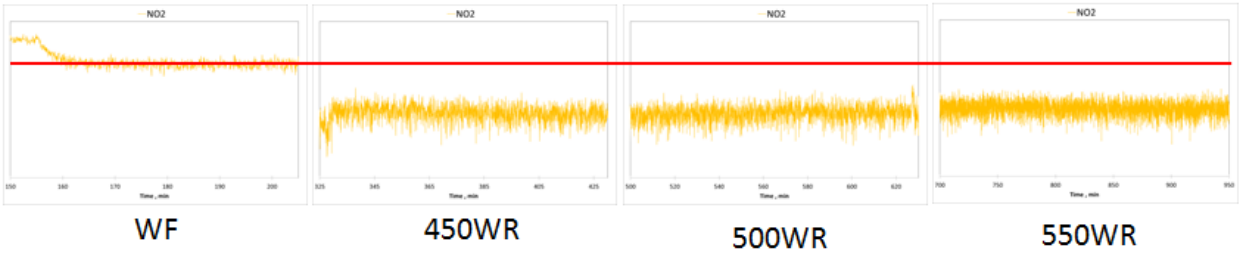

Figure 10: NO_2 Signal for Wet Runs on 0.3% Pd/SZ with CH_4 and NO_2

Due to the presence of carbon-carbon bonds, propane is also a viable option for the reduction of NO_x. This molecule is known to be easier to activate as a result of these bonds. In this experiment, the same 0.3% Pd/SZ catalyst is used. Temperatures from 250°C to 500°C were tested in 50°C intervals to identify the temperature ranges in which

these reactions occur. In this study, 40 mg of catalyst was loaded into the reactor. The feed was calibrated for the flow rates given in Table 4.

Table 4: Feed Flow Rates over 0.3% Pd/SZ for NO_2 Reduction

Component	Composition
C_3H_8	0.67%
O_2	10%
NO_2	2014 ppm
H_2O	7%
Total	25 ccm

The feed composition for this experiment has the same C:N ratio that was used with the previous experiment with methane. Conversion of propane was calculated as was done in the previous Pd/SZ studies. Tables A5 and A6 report the data collected by the Micro GC, along with corresponding concentrations and conversion of propane. Figure 11 shows the conversion of propane for dry and wet runs as a function of temperature.

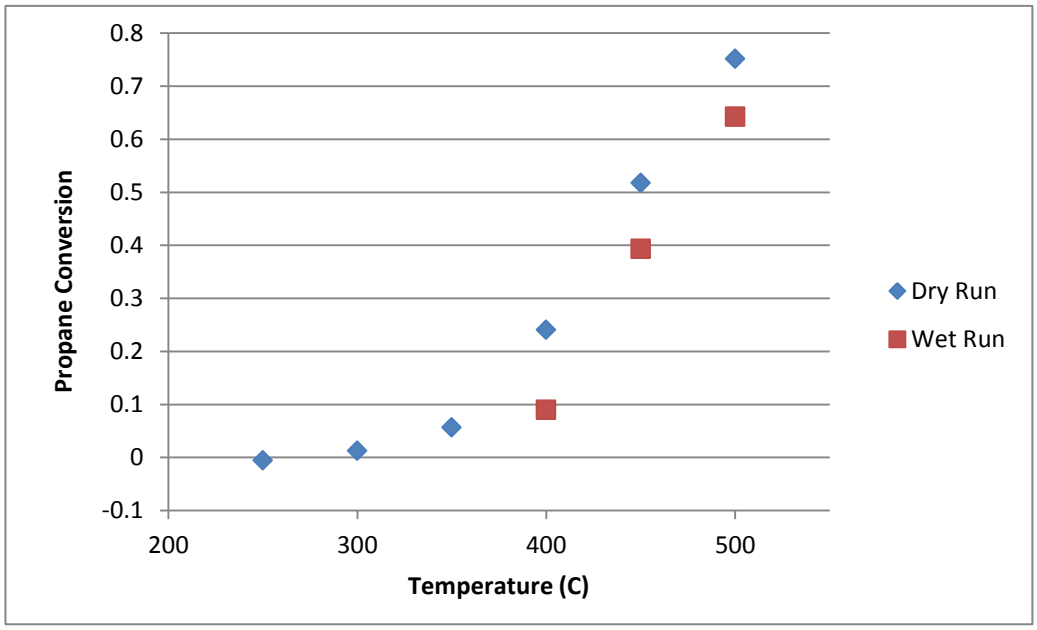

Figure 11: Fractional Conversion of Propane on 0.3% Pd/SZ with NO_2

As seen in this plot, conversions of propane in this system are lower than conversions of methane seen on the same catalyst. After observing a low conversion of propane at 250°C - 350°C under dry conditions, these trials were not performed under wet conditions. The paired t-test was then performed on the remaining data. This test yielded a p-value of 0.0045, indicating that water has a significant effect on the conversion of propane on this catalyst between 400°C and 500°C. The printout from this test can be seen in Figure B3.

The reduction of NO_2 was monitored with the MS. By measuring signal for both N_2 and NO_2, a qualitative assessment of the ability of this catalyst to reduce NO_2 with propane can be made. Figure 12 shows the nitrogen signal produced by the MS for the dry runs in this experiment.

Figure 12: N_2 Signal for Dry Runs on 0.3% Pd/SZ with C_3H_8 and NO_2

This figure shows an increase in the nitrogen signal with increasing temperature, as was seen on methane previously. This indicates that NO_2 was likely reduced in this experiment, releasing nitrogen in the process. This can be verified with the NO_2 signal, shown in Figure 13.

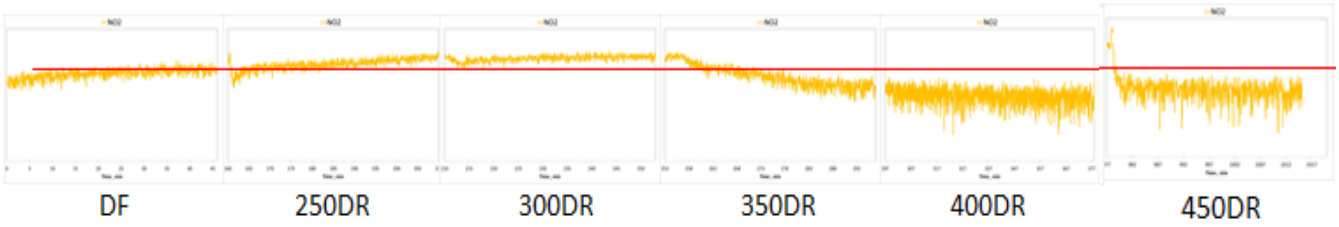

Figure 13: NO_2 Signal for Dry Runs on 0.3% Pd/SZ with C_3H_8 and NO_2

This data confirms that NO_2 is being reduced on this catalyst by propane. There is a gradual reduction in the amount of NO_2 present in the products as temperature increases from 350°C to 450°C, which agrees with the propane conversion results from Figure 12. Figure 14 shows the N_2 signal produced by the MS for the wet runs in this experiment. Due to an unknown error during data acquisition, many of the spectra collected were not deemed accurate and are excluded from this figure. The feed conditions and wet run from 400°C are reported here. This experiment may be later repeated to obtain MS data for these conditions.

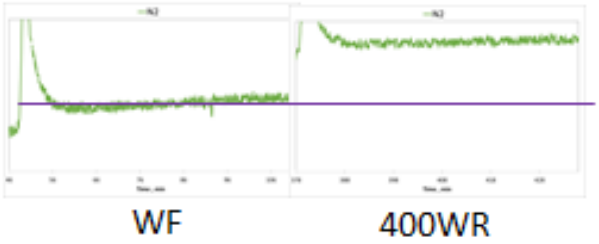

Figure 14: N_2 Signal for Wet Runs on 0.3% Pd/SZ with C_3H_8 and NO_2

The data from the 400°C run indicates that nitrogen is produced at this higher temperature in the reactor. This result is also seen at this temperature under dry conditions. It is again expected that this nitrogen production is a result of the reduction of NO_2. Figure 15 shows the NO_2 signal produced by the MS for the wet runs on this catalyst. Again, only the feed and 400°C results are included.

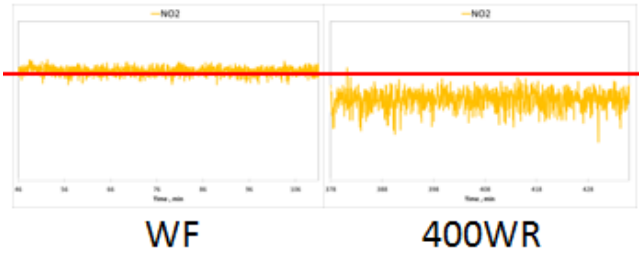

Figure 15: NO_2 Signal for Wet Runs on 0.3% Pd/SZ with C_3H_8 and NO_2

These results show a decrease in NO_2 signal at this elevated temperature, indicating that nitrogen was produced by the reduction of NO_2 on this catalyst. Additional experiments may be performed to quantify this reduction.

These NO_2 reduction experiments show that the conversion of propane were about 10%-15% greater than the conversion of methane under the same conditions, indicating that propane was more readily activated on this catalyst. These experiments should be repeated in order to give more confidence to this conclusion and better quantify the difference in hydrocarbon conversion. Both methane and propane showed an ability to reduce NO_2 on the Pd/SZ catalyst. Additional experimentation will aid in quantifying the extent of these reactions.

Oxidation of Hydrocarbons and Reduction of NO_2 on Pd/Oz

Experiments now focus on using osorb as a support for these palladium catalysts. In order to best mimic the sulfated zirconia support, osorb is also sulfated in this experiment. 10% palladium is then added to the osorb with the incipient wetness impregnation technique described previously. First, the temperature at which the oxidation of methane begins to occur on this catalyst must be determined. To do this, the reaction was performed without water at temperatures ranging from 250°C to 600°C in 50°C intervals. The system was charged with 40 mg of catalyst. Table 5 gives the feed composition sent to the reactor in this experiment.

Table 5: Feed Flow Rates over 10% Pd/SOz

Component	Composition
CH_4	1737 ppm
O2	10%
Total	20 ccm

Conversion of methane was calculated as was done in previous studies. Table A7 shows the data collected by the GC with corresponding concentrations of methane and carbon dioxide as well as methane conversion. Conversion is also plotted in Figure 16.

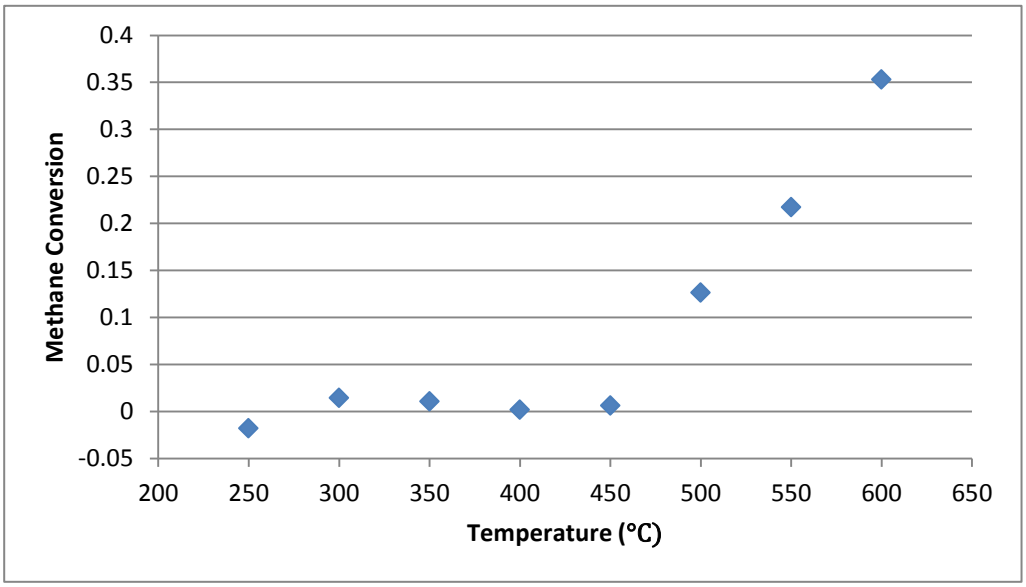

Figure 16: Conversion of Methane over 10% Pd/SOz

As shown by this plot, methane does not become active on this catalyst until somewhere between 450°C and 500°C. A carbon balance was also performed on these data to determine the fraction of carbon that leaves the reactor as methane or carbon dioxide compared to the methane in the feed. Table A8 shows the results of this balance and

Figure 17 shows the fraction of carbon measured as either carbon dioxide or methane in the runs as compared to the feed.

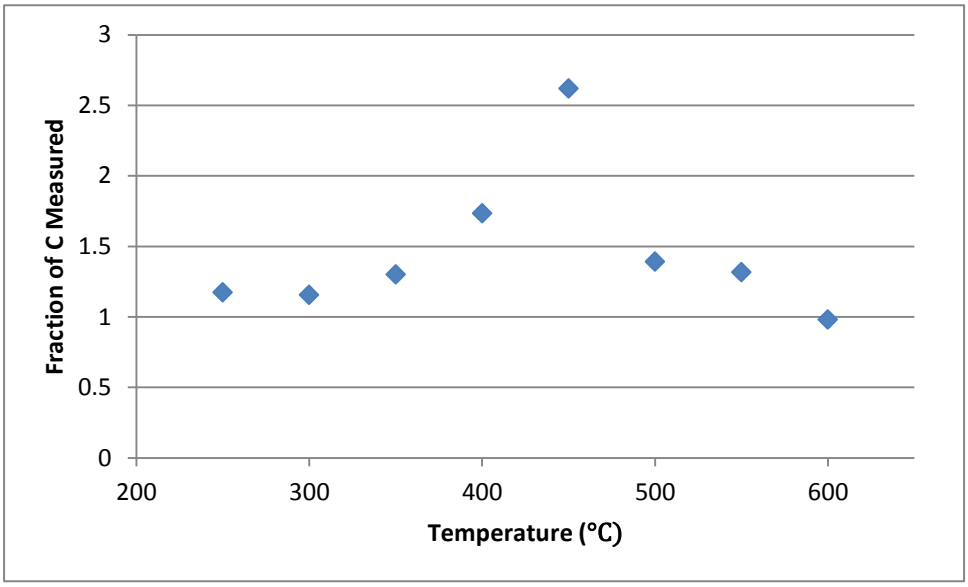

Figure 17: Fraction of Carbon Retained as CO_2 or CH_4 over 10% Pd/SOz

This result looks drastically different from previous results seen with the Pd/SZ catalyst. The peak at 450°C is much greater than one, indicating that there is carbon leaving the catalyst in the form of either methane or carbon dioxide. If these molecules are being generated from the catalyst surface, this material may see structure and/or function changes. Additional characterization of this catalyst was required to help explain this phenomenon.

A temperature programmed oxidation (TPO) experiment was performed on this new Pd/SOz catalyst. This characterization technique shows how the surface of the catalyst changes with temperature in oxidizing conditions, such as those seen in this reaction system. Figure 18 shows the reaction profile used in this experiment.

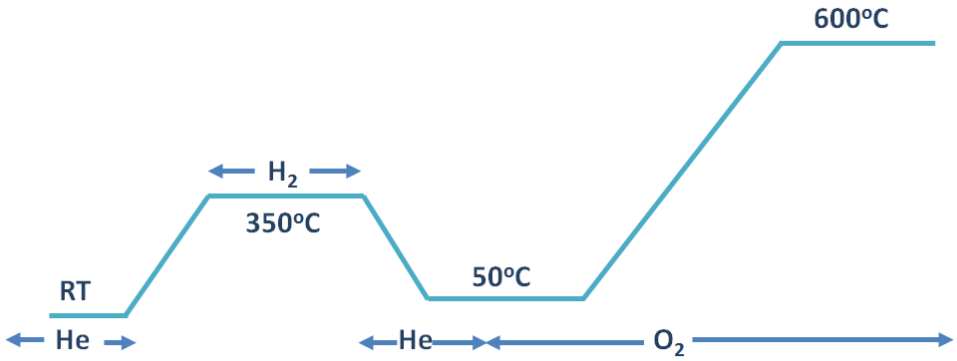

Figure 18: Temperature Programmed Oxidation of 10% Pd/SOz Reaction Profile

The catalyst is subjected first to hydrogen at 350°C to ensure that the catalyst is reduced. The sample is then cooled to 50°C under helium. Oxidation begins this temperature and the temperature is increased at a rate of 10°C per minute up to 600°C. Figure 19 shows the result of this characterization.

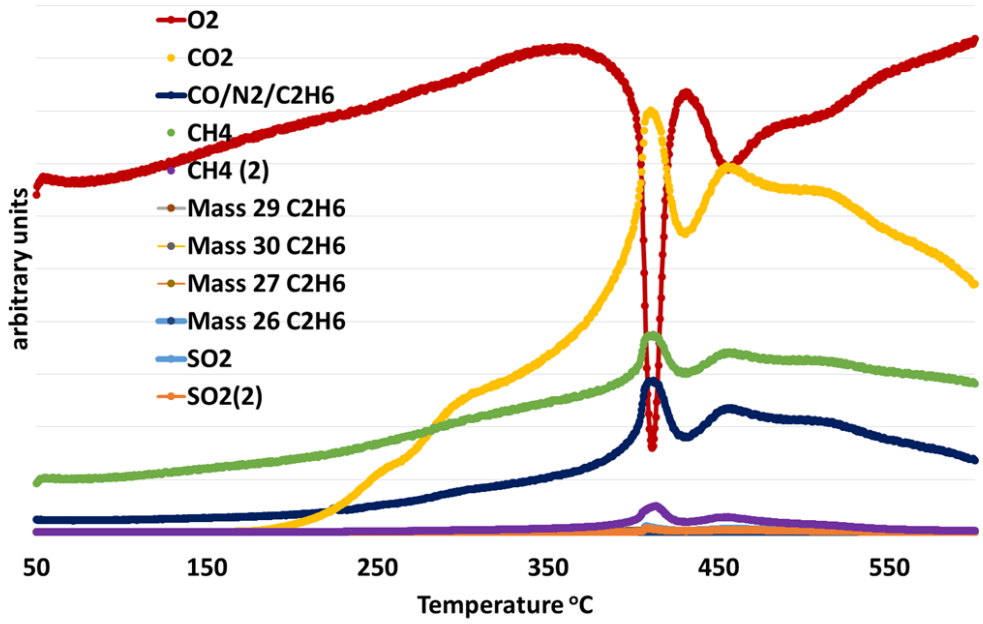

Figure 19: Results of TPO of Pd/SOz

As seen in the results, a change in the surface of this catalyst occurs slightly above 400°C. The formation of methane, ethane, SO_2, and CO_2 is observed at this temperature. This explains the results seen in the carbon balance previously performed on this catalyst. The formation of methane and carbon dioxide from carbon found in the catalyst occurs at temperatures between 400°C and 450°C in this TPO experiment, which is consistent with the carbon balance shown in Figure 18. The structure and characteristics of the resulting material are unknown at this time. Additional characterization may be performed to identify the new structure.

Due to the results of the sulfated osorb catalysts, another modification to the original material was made. This modification produces non-swellable osorb, which is intended to retain all other properties of osorb besides the ability to swell. 1% palladium was added to the non-swellable osorb with the incipient wetness impregnation procedure described previously. The ability of this catalyst to simultaneously oxidize methane and reduce NO_2 was first tested. Table 6 shows the feed composition used in this experiment.

Table 6: Feed Flow Rates over 1% Pd/Oz (non-swellable) with CH_4 and NO_2

Component	Composition
CH_4	2%
NO_2	2014 ppm
O_2	10%
H_2O	7%
Total	25 ccm

This new catalyst was tested with this feed at temperatures of 400°C to 550°C in 50°C intervals. The data collected by the Micro GC for methane and carbon dioxide concentrations, along with methane conversion, can be seen in Tables A9 and A10 for

dry and wet runs, respectively. Figure 20 shows these conversions as a function of temperature.

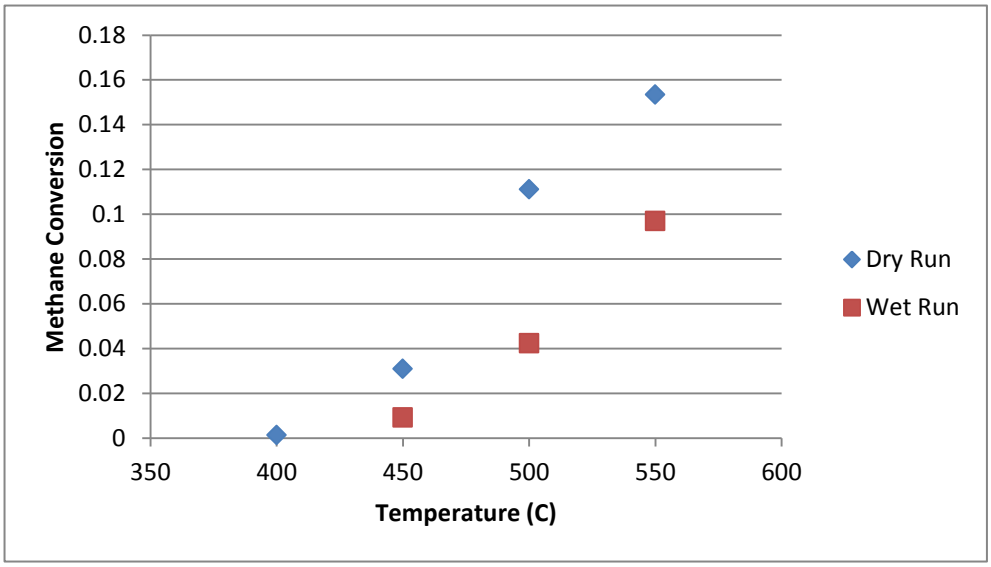

Figure 20: Conversion of Methane over 1% Pd/Oz (non-swellable)

After the first dry run at 400°C showed little conversion of methane, the wet run at this temperature was not performed. The same paired t-test was performed on the remaining data to see if there was an effect of water on the conversion of methane in this temperature range. JMP reported a p-value of 0.0367, indicating that the presence of water had a significant effect on the conversion of methane from 450°C to 550°C. A full printout of this test can be seen as Figure B4. A carbon balance was performed on the data collected by the Micro GC. A carbon balance was performed on the methane and carbon dioxide measured going in and out of the system to see if the balance closes with these species. Table A11 shows the results of this calculation. Figure 21 shows the carbon balance results for dry and wet runs in this experiment.

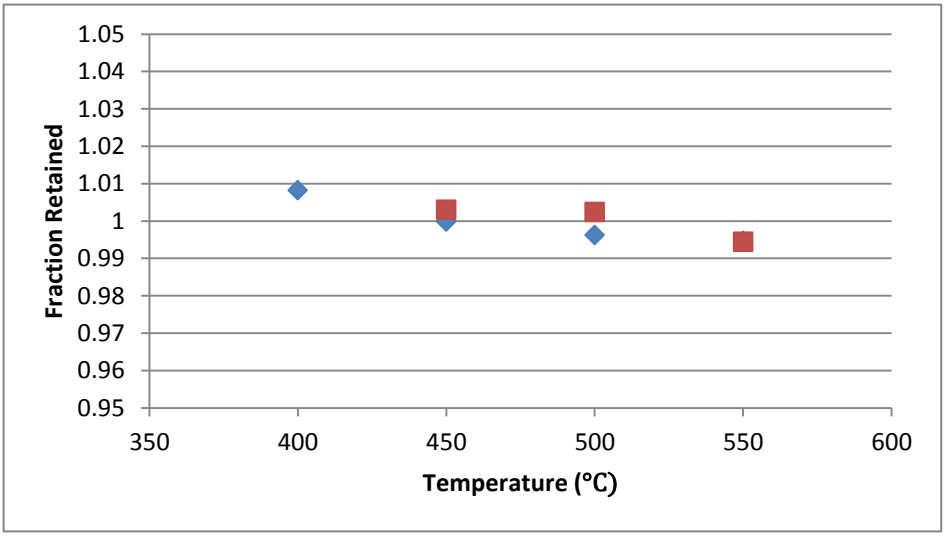

Figure 21: Carbon Balance over 1% Pd/Oz (non swellable) with CH_4 and NO_2

As seen in this figure, almost all carbon fed to the system is present as either methane or carbon dioxide after the reaction. It can therefore be assumed that the catalyst support is not seeing any changes in structure.

The MKS Cirrus mass spectrometer was again used in this experiment to give a qualitative assessment of the ability of this new catalyst to reduce NO_2. Figure 22 shows the signal generated by the MS for nitrogen in the dry runs on this catalyst.

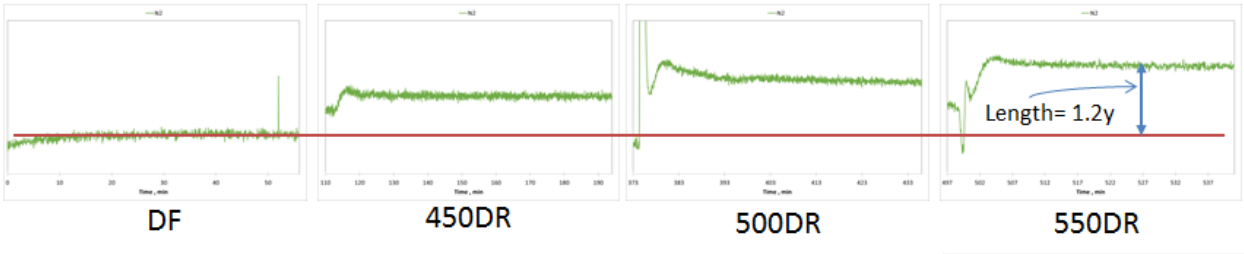

Figure 22: N_2 Signal for Dry Runs on 1% Pd/Oz (non-swellable) with CH_4 and NO_2

The nitrogen signal appears to increase with temperature on this catalyst. The production of nitrogen may be a result of the reduction of NO_2 on this catalyst. The height of the

signal at 550°C above the baseline is 1.2y (unitless). This value will be referenced later. To confirm that this nitrogen is a product of the reduction of NO_2, the signal of NO_2 is shown in Figure 23.

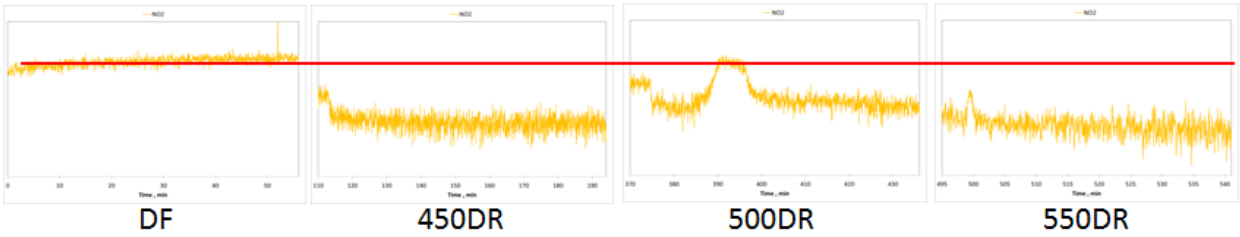

Figure 23: NO_2 Signal for Dry Runs on 1% Pd/Oz (non-swellable) with CH_4 and NO_2

The signal of NO_2 decreases with increased temperature for these runs, confirming that the nitrogen production seen was a result of the reduction of this molecule. For comparison, Figure 24 shows the nitrogen signal of the MS for the wet runs in this experiment.

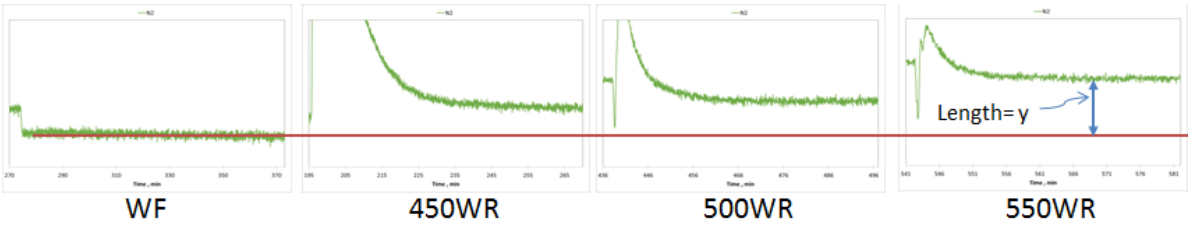

Figure 24: N_2 Signal for Wet Runs on 1% Pd/Oz (non-swellable) with CH_4 and NO_2

This data again shows that more nitrogen is found in the products of this reaction as temperature increases. The height of this signal at 550°C is 1.2y, so the ratio of nitrogen produced in the wet runs as compared to the dry runs is approximately 6:5. The reduction of NO_2 can be confirmed with the NO_2 signal for these experiments, shown in Figure 25.

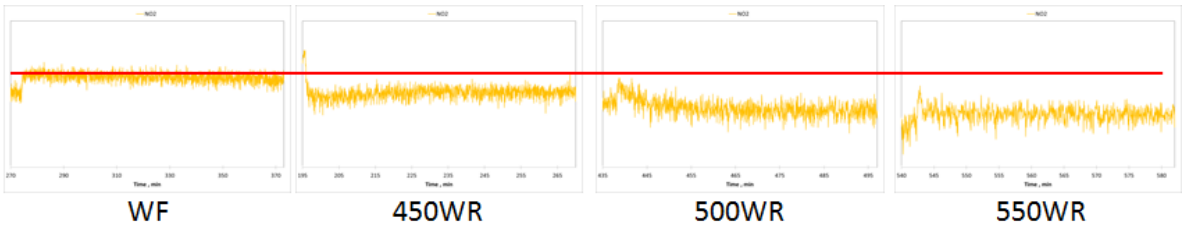

Figure 25: NO_2 Signal for Wet Runs on 1% Pd/Oz (non-swellable) with CH_4 and NO_2

The NO_2 signal decreases with increased temperature, confirming that NO_2 is being reduced with methane to form nitrogen. Additional experiments may be performed to better quantify the extent of this reaction.

Finally, the new Pd/Oz (non-swellable) catalyst was tested for its ability to reduce NO_2 with propane. As was done with the Pd/SZ catalyst, the carbon-nitrogen ratio was held constant between the experiments with methane and propane. Table 7 shows the feed composition used in this experiment.

Table 7: Feed Flow Rates over 1% Pd/Oz (non-swellable) with C_3H_8 and NO_2

Component	Composition
C_3H_8	0.67%
NO_2	2014 ppm
O_2	10%
H_2O	7%
Total	25 ccm

This catalyst was subjected to these conditions at temperatures from 350°C to 550°C in 50°C intervals. The data collected on propane and carbon dioxide from the Micro GC is summarized in Tables A12 and A13. Figure 26 shows the conversion of propane as a function of temperature for dry and wet runs.

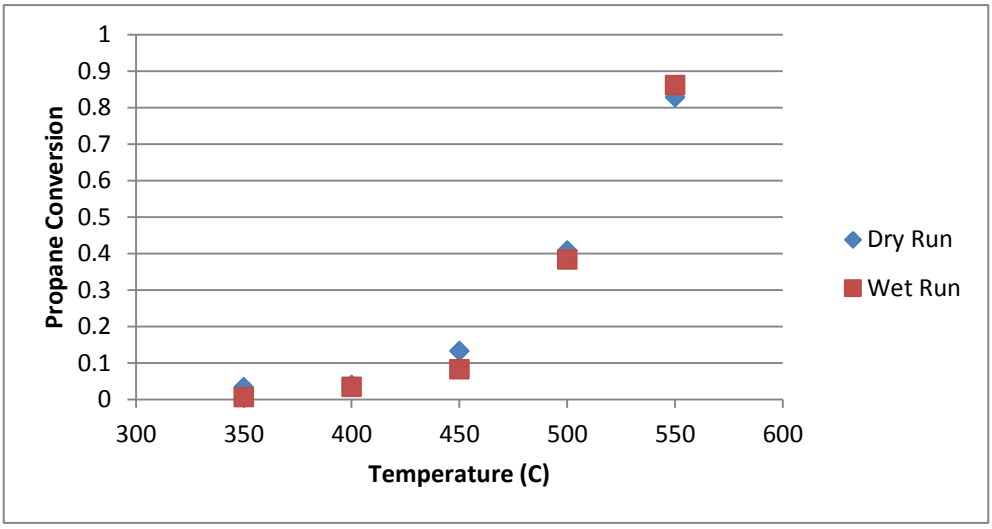

Figure 26: Conversion of Propane over 1% Pd/Oz (non-swellable)

Upon first inspection, it appears that the conversion of propane does not vary greatly between the dry and wet runs. To confirm this, a paired t-test was performed on these data in JMP. This calculation reported a p-value of 0.1746. A full printout of this test can be seen as Figure B5. This result indicates that water did not have a significant effect on the conversion of methane in this experiment. This result is likely due to the hydrophobicity of the osorb support. If water is not allowed into the pores by the support, it cannot access the active sites and inhibit this reaction. The MKS Cirrus was also used in this experiment for qualitative analysis of the nitrogen and NO_2 compositions of the products. Figure 27 shows the nitrogen signal generated by this experiment in the dry runs.

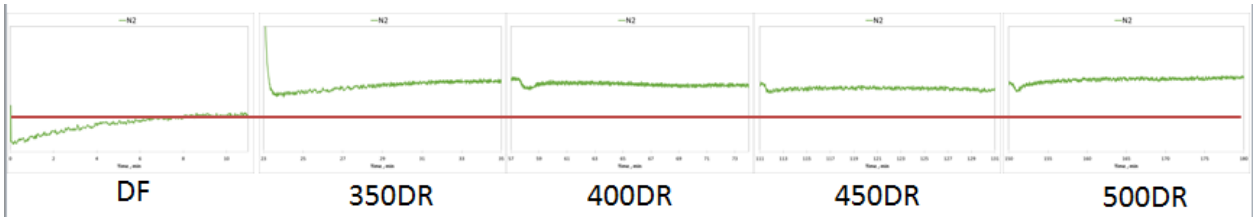

Figure 27: N_2 Signal for Dry Runs on 1% Pd/Oz (non-swellable) with C_3H_8 and NO_2

This signal shows increased nitrogen production as temperature increases on this catalyst. This is likely due to the reduction of NO_2 on this catalyst. This can be confirmed with the NO_2 signal, seen in Figure 28.

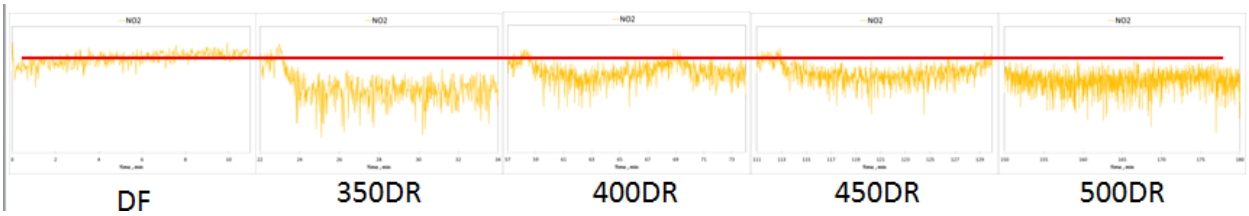

Figure 28: NO_2 Signal for Dry Runs on 1% Pd/Oz (non-swellable) with C_3H_8 and NO_2

Since the signal for NO_2 lies below the baseline at elevated temperatures over this catalyst, this catalyst is reducing NO_2 without water present. Figure 29 shows the nitrogen signal from the MS for the wet runs.

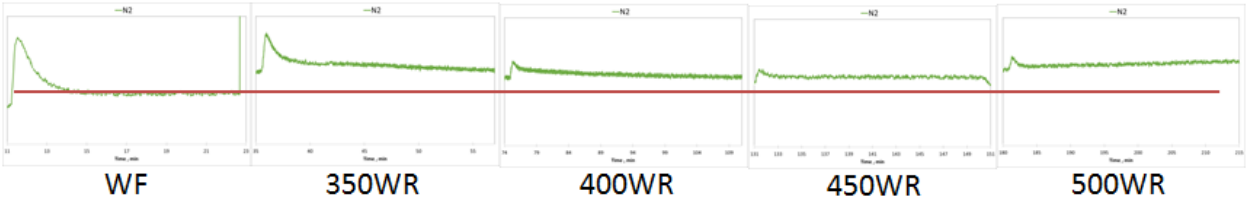

Figure 29: N_2 Signal for Wet Runs on 1% Pd/Oz (non-swellable) with C_3H_8 with NO_2

These signals also show an increase in nitrogen signal as temperature increased. This is likely due to the reduction of NO_2 with propane, forming nitrogen. Figure 30 shows the NO_2 signal produced in the wet runs of this experiment.

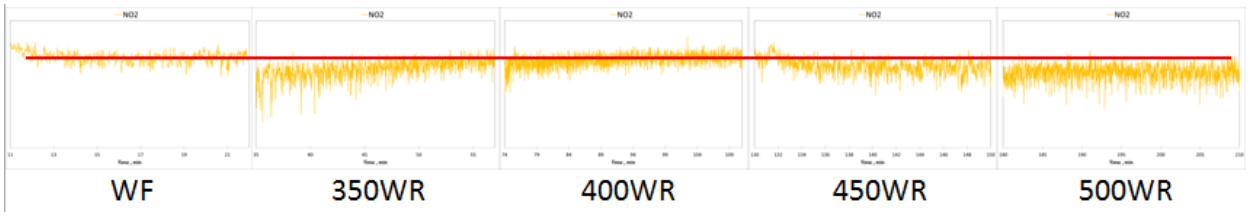

Figure 30: NO_2 Signal for Wet Runs on 1% Pd/Oz (non-swellable) with C_3H_8 and NO_2

The signal produced here decreases as temperature increases, indicating that NO_2 was reduced on this catalyst. Additional experiments may be performed to further quantify the extent of this reaction.

Recommendations and Future Work

There are several sources of error in these experiments that can be improved upon in later experiments. The osorb supported catalysts are new to this research and variability between batches of osorb has not yet been studied. As research continues, additional characterization will be performed on variations of the osorb material to learn more about its structural qualities as a catalyst support. Results of these characterization tests may lead to new ideas on how to make osorb a better support for this catalyst.

Currently, each trial in this research is stopped when the GC data suggests that the reaction has achieved steady state. As there is no rigorous definition of steady state used in regards to this data currently, different team members may interpret these data differently. A quantitative definition of steady state should be agreed on by the team in future research to avoid any bias seen in these data. Such a definition may require that the absolute or fractional difference in areas measured by the Micro GC meet certain criteria before the experiment can be continued with the next trial. This will remove any discrepancies between individual opinions of when the reaction has achieved steady state.

Another source of error in regards to the use of the Micro GC is related to the manual calculation of peak areas. The GC measures most peaks automatically, but certain peaks (specifically propane) must be regularly calculated with a manual integration tool in the software. The use of this tool requires the user to choose the region over which the peak is integrated. The way in which the user selects a region to integrate may be different than the way the program automatically integrates these peaks, leading to inconsistencies in these data. It is expected that these errors are small, but they are

difficult to quantify for analysis. This type of error may also be introduced when peaks overlap in the Micro GC printouts, requiring the user to approximate the regions that can be attributed to each peak.

Additional analysis can be performed on these data to extract a rate law with power law kinetics. Results of this analysis can be compared to literature results for both the oxidation and reduction reactions. Additionally, quantitative measurements can be taken on NO_x concentrations in the product streams to determine the exact conversion of NO_2 on these catalysts.

Conclusion

The presence of water was shown to have a significant effect on the conversion of methane on a palladium catalyst on sulfated zirconia in the absence of NO_2. This effect is well documented in the literature and a primary issue with the use of this catalyst in selective catalytic reduction applications. When this catalyst is subjected to a stream that also contains NO_2, mass spectrometry results show that reduction of this species occurs on this catalyst, resulting in the production of nitrogen. This catalyst also showed the ability to use propane as the reducing agent in the conversion of NO_2. However, water was shown to still have a significant effect on the conversion of both methane and propane on this catalyst.

Osorb is a new material that has interesting characteristics that make it a potentially beneficial support for use in selective catalytic reduction. Palladium was supported on sulfated osorb and placed in reaction conditions, resulting in an open carbon balance. Temperature programmed oxidation studies confirmed that at 400°C, this catalyst sees a chemical change that releases carbon containing species. As a result, the structure changes to an unknown form. A different variety of osorb, known as non-swellable osorb, was then tested for its ability as a support. This material showed stability at reaction temperatures to at least 550°C. This catalyst showed the ability to use both methane and propane as a reducing agent to convert NO_2 to nitrogen, carbon dioxide, and water. Using methane as the reducing agent, the presence of water was found to have a significant effect on conversion. However, the presence of water was found to have no effect on the conversion of propane on this catalyst in the presence of NO_2. This is one

hypothesized effect of the osorb support and is highly promising for future research with this material. Future work will focus on using this material for selective catalytic reduction in order to negate the effects of water on the palladium catalyst.

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Appendix A: Tables

Table A1: Experimental Methane Conversion on 0.3% Pd/SZ – Dry Run

Dry Runs					
Temperature (°C)	Area CH_4	PPM CH_4	Area CO_2	PPM CO_2	CH_4 Conversion
400	3681.4	1037.8	762.2	617.4	0.40
410	2726.8	768.7	1068.6	865.6	0.56
420	2259.0	636.8	1195.6	968.4	0.63
430	1629.6	459.4	1384.8	1121.7	0.74
440	1216.2	342.8	1513.4	1225.9	0.80
450	675.2	190.3	1667.0	1350.3	0.89
460	405.2	114.2	1757.6	1423.7	0.93
470	183.0	51.6	1811.0	1466.9	0.97
480	112.8	31.8	1830.6	1482.8	0.98
490	0.0	0.0	1845.0	1494.5	1.00
500	0.0	0.0	1859.0	1505.8	1.00

Table A2: Experimental Methane Conversion on 0.3% Pd/SZ – Wet Run

Wet Runs					
Temperature (°C)	Area CH_4	PPM CH_4	Area CO_2	PPM CO_2	CH_4 Conversion
400	6250.0	1761.9	124.4	100.8	0.05
410	6069.2	1710.9	211.6	171.4	0.08
420	5818.4	1640.2	272.4	220.6	0.12
430	5353.2	1509.1	419.8	340.0	0.19
440	4336.6	1222.5	722.6	585.3	0.34
450	3396.2	957.4	988.0	800.3	0.48
460	2383.8	672.0	1296.4	1050.1	0.64
470	1522.0	429.1	1545.8	1252.1	0.77
480	891.8	251.4	1744.4	1413.0	0.86
490	509.6	143.7	1864.2	1510.0	0.92
500	208.3	58.7	1955.5	1584.0	0.97

Table A3: Experimental Methane Conversion on 0.3% Pd/SZ with NO_2 – Dry Runs

Dry Runs					
Temperature (°C)	Area CH_4	PPM CH_4	Area CO_2	PPM CO_2	CH_4 Conversion
450	63374.2	17865.2	2998.2	2428.5	0.14
500	49115.2	13845.6	7287.0	5902.5	0.33
550	31558.6	8896.4	12501.4	10126.1	0.57

Table A4: Experimental Methane Conversion on 0.3% Pd/SZ with NO_2 – Wet Runs

Wet Runs					
Temperature (°C)	Area CH_4	PPM CH_4	Area CO_2	PPM CO_2	CH_4 Conversion
450	72871.2	20542.4	1891.0	1531.7	0.08
500	58994.6	16630.6	6055.2	4904.7	0.25
550	41163.6	11604.0	11355.0	9197.6	0.48

Table A5: Experimental Propane Conversion on 0.3% Pd/SZ with NO_2 – Dry Runs

Dry Runs					
Temperature (°C)	Area C_3H_8	PPM C_3H_8	Area CO_2	PPM CO_2	C_3H_8 Conversion
250	10092.6	5651.9	80.6	65.3	-0.01
300	9914.6	5552.2	393.8	319.0	0.01
350	9471.8	5304.2	1610.9	1304.8	0.06
400	7621.0	4267.8	5733.5	4644.1	0.24
450	4842.4	2711.7	11930.0	9663.3	0.52
500	2495.4	1397.4	18657.8	15112.8	0.75

Table A6: Experimental Propane Conversion on 0.3% Pd/SZ with NO_2 – Wet Runs

Wet Runs					
Temperature (°C)	Area C_3H_8	PPM C_3H_8	Area CO_2	PPM CO_2	C_3H_8 Conversion
400	9137.0	5116.7	4063.0	3291.0	0.09
450	6089.8	3410.3	10873.5	8807.5	0.39
500	3591.2	2011.1	16246.1	13159.4	0.64

Table A7: Experimental Methane Conversion on 10% Pd/SOz

Temperature (°C)	Area CH_4	PPM CH_4	Area CO_2	PPM CO_2	CH_4 Conversion
250	6281.0	1770.6	333.0	269.7	-0.02
300	6081.0	1714.2	362.0	293.2	0.01
350	6104.0	1720.7	666.0	539.5	0.01
400	6158.0	1735.9	1580.0	1279.8	0.00
450	6130.0	1728.0	3491.0	2827.7	0.01
500	5389.0	1519.2	1111.0	899.9	0.13
550	4829.0	1361.3	1144.0	926.6	0.22
600	3991.0	1125.1	718.0	581.6	0.35

Table A8: Fraction of Carbon Retained as CO_2 or CH_4 over 10% Pd/SOz

Temperature (°C)	Fraction Carbon Measured
250	1.17
300	1.15
350	1.30
400	1.73
450	2.62
500	1.39
550	1.32
600	0.98

Table A9: Experimental Methane Conversion on 1% Pd/Oz (non-swellable) – Dry Run

Dry Runs					
Temperature (°C)	Area CH_4	PPM CH_4	Area CO_2	PPM CO_2	CH_4 Conversion
400	72715.0	20498.4	247.0	200.1	0.00
450	70565.0	19892.3	781.0	632.6	0.03
500	64724.0	18245.7	2723.0	2205.6	0.11
550	61644.0	17377.4	3763.0	3048.0	0.15

Table A10: Experimental Methane Conversion on 1% Pd/Oz (non-swellable) – Wet Run

Wet Runs					
Temperature (°C)	Area CH_4	PPM CH_4	Area CO_2	PPM CO_2	CH_4 Conversion
400	-	-	-	-	-
450	78240.0	22055.9	344.0	278.6	0.01
500	75615.0	21315.9	1240.0	1004.4	0.04
550	71306.0	20101.2	2528.0	2047.7	0.10

Table A11: Fraction of Carbon Retained as CO_2 or CH_4 over 1% Pd/Oz (non-swellable)

Temperature (°C)	Fraction of C Measured – Dry Run	Fraction of C Measured – Wet Run
400	1.01	-
450	1.00	1.00
500	1.00	1.00
550	0.99	0.99

Table A12: Experimental Propane Conversion on 1% Pd/Oz (non-swellable) – Dry Run

Dry Run					
Temperature (°C)	Area C_3H_8	PPM C_3H_8	Area CO_2	PPM CO_2	C_3H_8 Conversion
350	10354.2	5798.4	1545.4	1251.8	0.03
400	10283.2	5758.6	1167.6	945.8	0.04
450	9288.0	5201.3	2496.2	2021.9	0.13
500	6344.4	3552.9	9458.4	7661.3	0.41
550	1841.8	1031.4	19891.2	16111.9	0.83

Table A13: Experimental Propane Conversion on 1% Pd/Oz (non-swellable) – Wet Run

Wet Run					
Temperature (°C)	Area C_3H_8	PPM C_3H_8	Area CO_2	PPM CO_2	C_3H_8 Conversion
350	11306.6	6331.7	663.6	537.5	-0.06
400	10983.4	6150.7	505.2	409.2	-0.03
450	10439.2	5846.0	1425.4	1154.6	0.03
500	7021.0	3931.8	9535.4	7723.7	0.34
550	1580.4	885.0	21608.6	17503.0	0.85

Appendix B: Figures

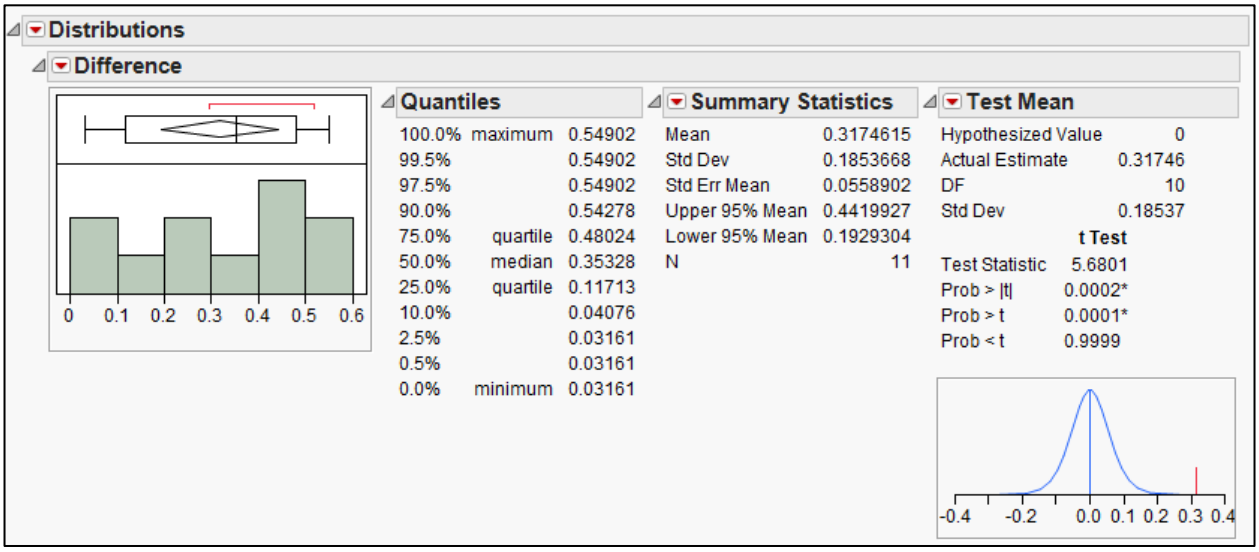

Figure B1: JMP for Paired t-Test from 0.3% Pd/SZ

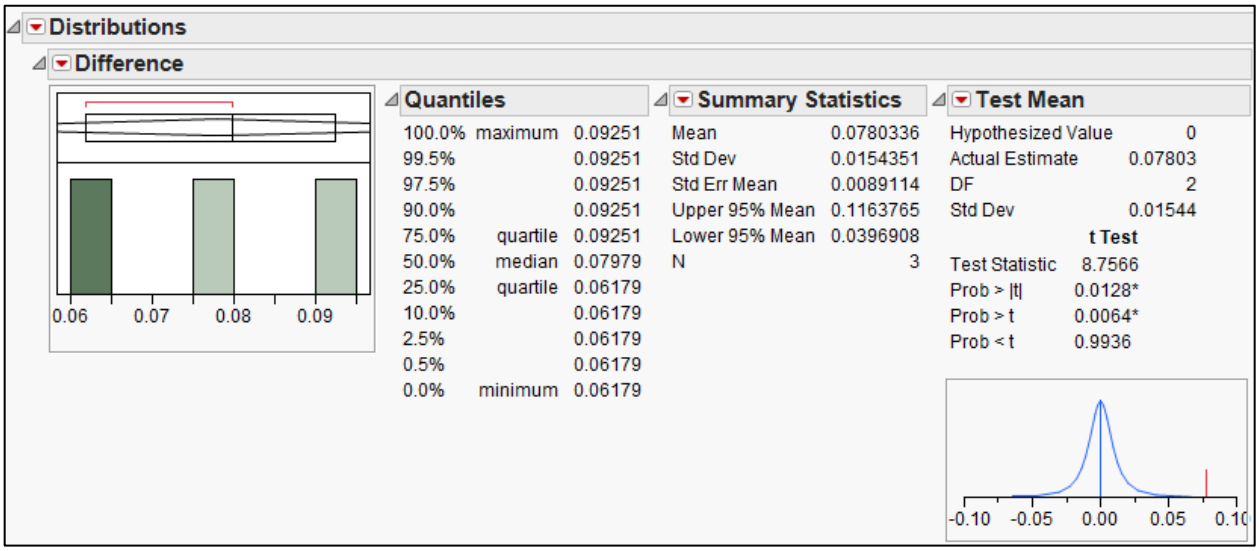

Figure B2: JMP for Paired t-Test from 0.3% Pd/SZ with CH_4 and NO_2

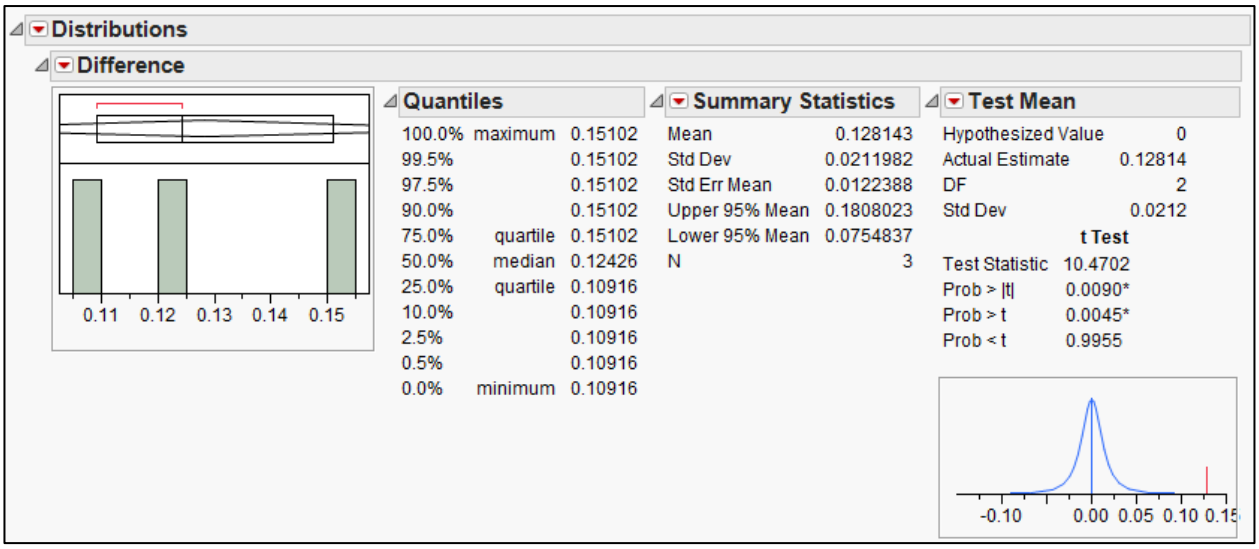

Figure B3: JMP for Paired t-Test from 0.3% Pd/SZ with CH_4 and NO_2

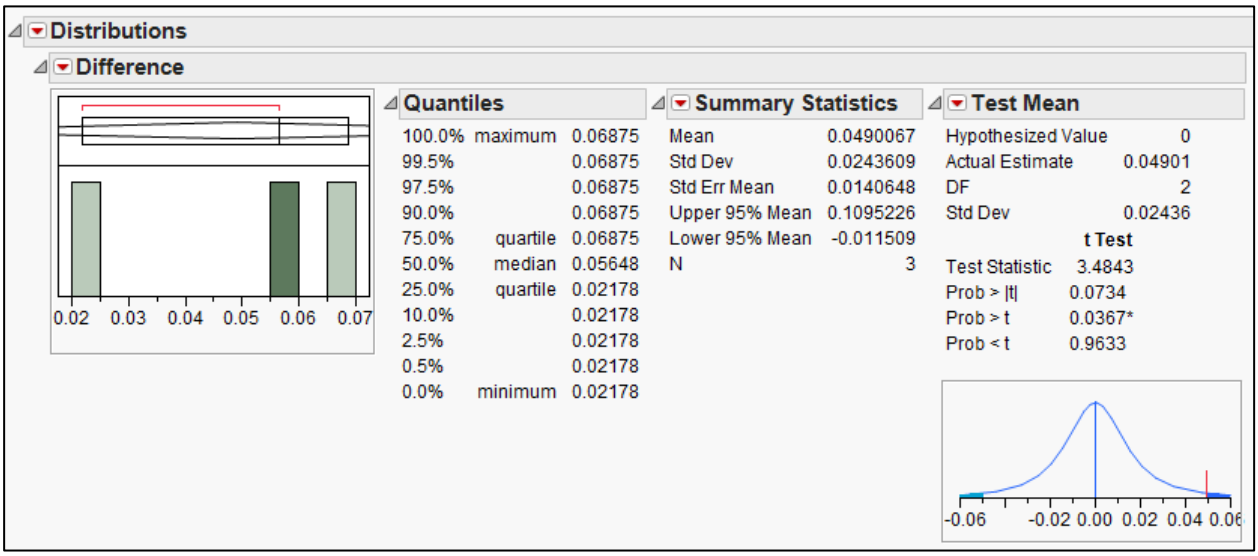

Figure B4: JMP for Paired t-Test from 1% Pd/Oz (non-swellable) with CH_4 and NO_2

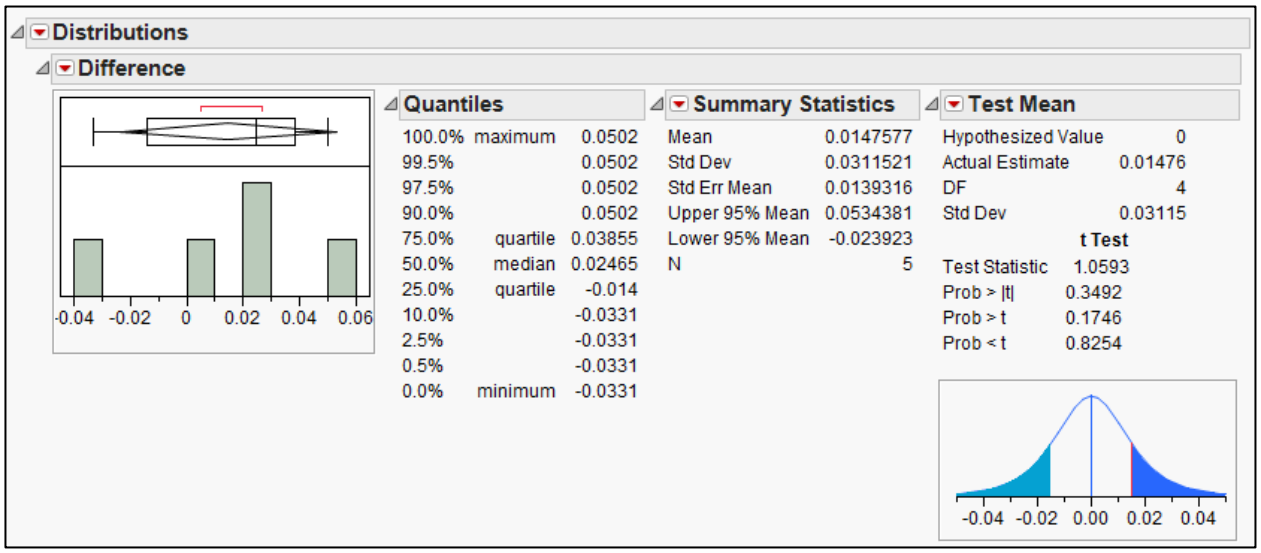

Figure B5: JMP for Paired t-Test from 1% Pd/Oz (non-swellable) with C_3H_8 and NO_2